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THE POSSIBLE ROLE OF HYDROGEN IN STRESS-CORROSION CRACKING OF TITANIUM ALLOYS

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ABSTRACT

The various mechanisms that have been put forward to explain stress-corrosion cracking are briefly summarized. The experimental observations of stress-corrosion cracking in titanium alloys in widely different environments are discussed. Evidence from the literature for and against the possibility that hydrogen plays a role in the stress-corrosion cracking of titanium alloys is documented. An experimental approach is outlined in an attempt to establish if environmental cracking in titanium alloys in specific environments is due mainly to a stress-corrosion mechanism or to a process similar to hydrogen embrittlement.

INTRODUCTION

The enormous emphasis in recent years on stricter material requirements for space exploration, deep-sea diving vessels, and high-speed aircraft has increased the importance of the problem of stress-corrosion cracking. High-strength materials are more susceptible to purely mechanical fast fracture. Many of them are also much more susceptible to stress-corrosion cracking in diverse environments. Even worse is the fact that the rate of growth of the stress-corrosion cracks in the high-strength materials is much faster than in lower strength alloys.

The combination of high strength-to-weight ratio and excellent corrosion resistance to a wide range of environments, reported by earlier workers, made titanium and its alloys attractive for a variety of applications. In recent years, however, stress-corrosion failures have been reported, first in laboratory conditions and more recently under service conditions.

There is some confusion in the literature regarding the exact definition of the term "stress-corrosion cracking." The terms "environmental cracking," "delayed fracture," "subcritical crack growth," and others have also been used. We shall use the term "stress-corrosion cracking" to designate failures that require conjointly a tension stress and a specific environment. A workable theory should include both factors in the fracture mechanism.

The initiation and propagation of stress-corrosion cracks can often be by distinctly different mechanisms. Several titanium alloys are good examples; e.g., they do not form corrosion pits at room temperature in sea water but are quite susceptible to the propagation of stress-corrosion cracks in the same environment.

Two schools of thought have evolved concerning stress-corrosion cracking—one favoring electrochemical dissolution concepts and the other, brittle-crack-step concepts. Attempts have also been made to distinguish stress-corrosion cracking from hydrogen cracking, in which the cause of fracture is directly related to hydrogen that is already present, or that enters the metal lattice through discharge of H^+ at the metal surface. Some features of such hydrogen cracking are similar to those of stress-corrosion cracking, but it has been suggested (1) that the causes differ, at least in detail. Cathodic polarization, for example, accelerates hydrogen cracking but inhibits stress-corrosion cracking. But it is far from certain from the data available in literature whether a clear-cut distinction can always be made between stress-corrosion cracking and hydrogen embrittlement, which often occur in the same environment.

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THEORIES OF STRESS-CORROSION CRACKING

The complexity of variables in the phenomenon of stress-corrosion cracking provides sufficient evidence that the mechanism is not simple, nor is it easily derived. Both the chemistry and the metallurgy of stressed metals actively undergoing fracture on exposure to damaging environments are not well understood. In the meantime, any successful working hypothesis should account for the following experimental observations:

1. Pronounced specificity of environments required for stress-corrosion cracking of many metals;
2. Greater resistance or immunity of pure metals;
3. Inhibiting (2) effect of extraneous anions;
4. Effect of structure and grain size.

Several theories have been proposed, but there are often elements of speculation and no one of them has been demonstrated beyond a doubt. Current theories usually resolve themselves into one of two mechanisms: (1) *Electrochemical*, including oxide film rupture or tubular corrosion pit modifications, or (2) *Stress sorption cracking* involving surface energy reduction by adsorbed components of the environment.

There are some indications (1) that cracking by either mechanism is related to pile-up of dislocations at barriers of one kind or another. The effect of increasing grain size in decreasing fracture stress is strong support of this idea. Furthermore, it has been suggested that unless the imperfections accumulate in suitable patterns along slip planes or grain boundaries, stress-corrosion cracking is not likely to occur. The imperfections, e.g., stacking faults or aggregates of dislocations, may accelerate diffusion and transport of impurity and alloy atoms to the imperfection arrays, causing localized segregation. This can account for resultant preferential dissolution by the electrochemical mechanism, or in turn the composition gradient may favor

adsorption of specific components of the environment, followed by reduction of surface energy.

ELECTROCHEMICAL THEORY

Dix (3) and Mears and Brown (4) were apparently the first to propose that a prerequisite for stress-corrosion cracking is the existence of a localized anodic path in the material. Thus, in the presence of a corrosive aqueous environment and a tension stress, a galvanic cell is set up in which the anodic path is preferentially attacked. The base of the resulting corrosion crevice then becomes the site of stress concentrations, which were thought to cause the metal to "tear apart by mechanical action." Support of this view was derived from potential measurements showing that intergranular, crack-sensitive paths in various aluminum alloys, as well as in some other metals, were anodic to grains. The electrochemical mechanism, with certain modifications depending on the metal, was elaborated by U. R. Evans (5), R. N. Parkins (6), T. P. Hoar (7), L. Graf (8), and others.

Keating (9) suggested that stress-corrosion cracks are formed by mechanical fracture, the propagation of which is interrupted periodically by barriers that require chemical dissolution before the crack can proceed. But the observation (10) that removal of the damaging environment from a crack, followed by further extension of the metal, resulted in ductile behavior casts doubt on the generality of Keating's argument.

The oxide film rupture theory, first mentioned by Dix, was modified and extended by Logan (11), by Forty and Humble (12), and by McEvily and Bond (13). The common point of view is that a film of brittle surface corrosion product ruptures under stress, allowing progressive exposure of metal underneath to further chemical attack. Support of this mechanism was derived from potential measurements or from visual or microscopic examination of metals that had undergone stress-corrosion cracking. Such a mechanism, though certainly applicable in special cases, is

probably not general because (1) stress-corrosion cracking in alpha brass is observed in the absence of visible films, e.g., in alkaline NH_4OH , (2) pure metals on which brittle or cathodic corrosion products form quite readily are immune, and (3) tarnished metals in air on which equally brittle films exist do not fail.

A modified electrochemical-mechanical model was suggested by Pickering and Swann (14). They proposed that an observed network of tubular corrosion pits forming along preferred paths such as active slip planes could account for cracking by ductile fracture of the tenuous walls of numerous adjacent pits.

Proponents of the electrochemical dissolution theories have yet to explain how dissolution is concentrated at the crack tip and to account for the high rates of cracking commonly observed. Since plastic deformation is concentrated ahead of the crevice, it would be attractive to attribute the rapid dissolution to the higher energy of the deformed material, i.e., to the fact that deformed metal is anodic relative to the undeformed metal. However, it is generally considered that the effect of elastic strain energy is too small to account for a significant increase in dissolution rate.

The main general support of the electrochemical mechanism is contributed by potential measurements and the inhibiting effect of cathodic polarization. Unexplained is the required specificity of environments for cracking, the inhibiting effect of extraneous ions, and (as will be discussed later) the susceptibility of titanium alloys to stress-corrosion cracking in environments such as nitrogen tetroxide and methanol, which are not electrolytes.

STRESS-SORPTION CRACKING

Cracking by this mechanism is supposed to proceed not by chemical or electrochemical dissolution of metal at the tip of the crack, but by weakening of already strained atomic bonds through adsorption of the environment or its constituents. The surface energy of the metal is

said to be reduced as a result of the adsorption process. This is essentially the mechanism that Petch and Stables (15) first suggested for hydrogen cracking of steels and that was later emphasized by Uhlig (16) and by Coleman, Weinstein, and Rostoker (17) as being applicable to stress-corrosion cracking of metals and alloys.

Langmuir (18) showed that only a monolayer of adsorbate is necessary to decrease affinities of surface atoms for themselves or for their environment, specifically adsorbed species chemically bonded (chemisorbed) to the surface being especially effective in this regard. Crack initiation is thought to involve such decrease in surface affinities, with the distinction that only those specific adsorbates are effective that reduce the attractive forces between adjoining metal atoms, at the extreme root of a notch, subject to tensile stress and experiencing some plastic deformation.

In addition to explaining the fracture of steels containing hydrogen, crack propagation aided by adsorption has been suggested as explaining the fracture of glass (19) and of solid metals by liquid metals (20), and the stress cracking of plastics by specific organic solvents (21). Obviously, electrochemical reaction is not a necessary part of such failures even though many other features resemble stress-corrosion cracking in aqueous media.

The general support for the stress-sorption cracking mechanism comes from the observation of:

1. The specificity of environments causing cracking because chemisorption is also specific.
2. The inhibiting effect of extraneous anions and of cathodic protection. Anions in sufficient concentration tend, by mass action, to displace (22) adsorbed damaging species. Alternatively, they may shift the corrosion potential into regions where damaging species do not adsorb. For similar reasons, cathodic polarization is generally effective because the potential is shifted into regions where

- damaging species (anions) cannot adsorb.
3. The cracking of nonmetals by specific environments and of metals by specific liquid metals.

STRESS-CORROSION CRACKING OF TITANIUM ALLOYS

The susceptibility of titanium alloys to stress-corrosion cracking when exposed to red fuming nitric acid (23), various aqueous solutions (24, 25), and sodium chloride at elevated temperatures (26) has been recognized for some time. More recently, it has been observed that stress-corrosion failures also occur in nonaqueous liquids, e.g., in nitrogen tetroxide (27) and methanol-hydrochloric acid solutions (28).

The Apollo tankage failure caused by methanol has triggered fresh interest in the study of the stress-corrosion susceptibility of titanium alloys in nonaqueous environments. At Naval Research Laboratories it has been found (29) that stress-corrosion cracks may be initiated in stressed smooth-specimen titanium alloys by methanol, ethylene glycol, and absolute ethyl alcohol; the aggressiveness decreases in the order given. With precracked specimens, apparently all the alcohols degrade the threshold stress intensity level to values less than half the measured dry fracture toughness index K_{IC} . The straight-chain saturated hydrocarbons—propane, hexane, and heptane—degrade the threshold stress intensity level to about the same level as the longer-chain alcohols.

THE ROLE OF HYDROGEN

Today there are several hundred papers dealing with the stress-corrosion cracking of titanium alloys in a diversity of environments encompassing both electrolytes and nonelectrolytes. In spite of this there is great divergence of opinion regarding the nature of stress corrosion in titanium alloys. Part of the difficulty in arriving at a certain conclusion arises from the complexity of the stress-corrosion process itself. This is

particularly apparent in the very conflicting conclusions that have been deduced by different authors regarding the role of hydrogen in the stress-corrosion cracking of titanium alloys.

It is intended to briefly summarize in this section the experimental evidence for and against the importance of hydrogen in stress-corrosion cracking, primarily in alpha titanium alloys.

EVIDENCE SUPPORTING A HYDROGEN MECHANISM

In hot-salt corrosion tests, Rideout et al. (30) suggested that adsorption of corrosion-produced hydrogen promotes cracking. Using radioactive tracer techniques, they found a high hydrogen concentration in the crack areas. They further observed, under the hot-stage microscope, that although corrosion stains appear almost immediately around salt crystals, cracking does not initiate until about 1-1/2 hours later. The cracks appear abruptly and propagate stepwise by abrupt extensions. The same study also confirmed the fact that no cracking could be initiated unless moisture was present.

There is increasing evidence to show that hydrogen may also be playing a role in the methanol cracking mechanism. Scully (32), using transmission electron microscopy, has observed hydride formation along alpha-beta phase boundaries of a Ti-5Al-2.5Sn alloy after cracking in methanol. He also found that hydride formation occurred only in susceptible alloys and in those environments that cause stress-corrosion cracking. The electron micro-auto-radiography work of Tiner (31) shows that hydrogen in quantities of less than 50 ppm (as tritium) introduced into titanium alloys preferentially segregates to the beta phase in alpha-beta alloys and to the grain boundaries in all-alpha alloys but is dispersed quite uniformly in beta-type alloys. According to Scully, the important electrochemical requirement for cracking is a delay in repassivation permitting the rapid formation of a hydride precipitate. During the repassivation

process, hydrogen is discharged on the metal surface at the tip of the crack, enters the metal, and a hydride is nucleated. Under increasing stress and/or continuing hydrogen discharge, crack propagation proceeds by continuous formation of hydride phase and fracture associated with it.

Sedriks et al. (33) investigated the stress-corrosion cracking of Ti-5Al-2.5Sn alloy in methanol vapor-air atmospheres. Their experimental observation that embrittlement can be eliminated by vacuum annealing suggests that some form of hydrogen-induced embrittlement is involved. It is unlikely that any other atomic species, which could be generated by exposure to methanol vapor-air atmosphere, would have sufficient mobility at room temperature to diffuse through the metal to the observed extent. It is not certain whether failure results from hydride formation or from the presence of atomic or molecular hydrogen in the lattice.

A tentative explanation based on release of hydrogen has been proposed by the investigators at The Naval Research Laboratory (29) on stress-corrosion cracking of titanium alloys in alcohol or straight-chain saturated hydrocarbons. The primary alcohols may initiate and propagate cracks by reacting with a fresh titanium alloy surface to yield an alkoxide and hydrogen. In the case of tertiary alcohols and alkanes, which do not cause crack initiation, the contact with a fresh titanium alloy surface may cause them to crack (petrochemically) to yield unsaturated hydrocarbons and hydrogen. Since in either case hydrogen is released, it is suspected to be a cause of embrittlement.

Recently Sandoz (34) has shown a relationship between the hydrogen content of certain titanium alloys and the susceptibility to stress-corrosion cracking of these alloys in salt water. His work on Ti-8Al-1Mo-1V alloy containing 48-50 ppm hydrogen showed that "delayed fractures" in dry air and dry helium occur at stress intensity values approximately half the values found when specimens are loaded to fracture. Threshold stress intensity values are found below which slow crack

growth and delayed fracture do not occur. The electron fractographs of the nonenvironmental cracks resemble somewhat those of stress-corrosion cracking of the same alloys in salt water. He further showed that vacuum annealing of the alloy to remove hydrogen indicates that K_{IH} (the value of K_{ISCC} in dry air) varies inversely with hydrogen content. However, these vacuum annealing experiments produced essentially no changes in the values of K_{ISCC} in environments other than dry air.

EVIDENCE AGAINST A HYDROGEN MECHANISM

Titanium alloys would crack in a stress-corrosion test in oxygenated N_2O_4 , as was shown when a Ti-6Al-4V tank filled with N_2O_4 ruptured during a pressure test at Bell Aerosystems Co. Since then, cracking in similar types of environment has been noted by Sedriks et al. (33) and Boyd (35). They pointed out that it is difficult to see how an embrittling mechanism involving hydrogen could occur in N_2O_4 and suggested instead that stress-corrosion cracking during exposure to oxygenated N_2O_4 occurs by repeated formation and fracture of a brittle oxide film.

Haney et al. (36), as well as Sedriks et al. (33), investigated the time-to-failure of titanium alloys in methanol-halogen-water environments. In general, impressed anodic currents were found to decrease the time-to-failure, whereas small cathodic currents markedly increase the time-to-failure. This behavior is consistent with electrochemical attack along an active path, not with a mechanism involving hydrogen embrittlement. Similar studies (35) of titanium alloy exposed to sea water have shown that an actively propagating crack can be stopped by the application of a cathodic potential. However, contrary to most cases of stress-corrosion cracking, the application of an anodic potential does not appear to significantly increase susceptibility to cracking.

Potential measurements made during step loading of susceptible Ti-8Al-1Mo-1V alloy specimens in sea water show potential peaks after each load is

applied, which then return in a fairly short time to the potential measured before the load was applied (37). When a sufficient load is added, however, the potential becomes very active and there is no indication of repassivation. It may be recalled that Scully (32) suggested that when exposing a bare titanium surface under conditions of high strain a hydride is probably produced that would overcome the strong repassivation tendency.

Beck and Blackburn (38) studied the stress-corrosion cracking of Ti-8Al-1Mo-1V in aqueous halide solutions and proposed a halide ion current near the crack tip. They concluded that the rate of hydrogen ion discharge within the tip zone must be small since, if the hydrogen ion current were of comparable value to the halide ion current, there would be no potential gradient. This would appear to exclude the hydride mechanism. However, they did not specify the mechanism of interaction of the environment with the metal. They also reported that a recycling of halide ions by displacement or hydrolysis occurs near the crack tip. Hydrolysis of the initially formed titanium halide occurs with the generation of hydrogen ions that was suggested to be reduced at another position in the crack. It is not clear from their work why, if hydrolysis does occur, the hydrogen that is generated should not have sufficient mobility to cause stress-corrosion cracking by a hydrogen mechanism. Internal friction measurements have already indicated (39) that stress-induced interstitial diffusion of hydrogen in titanium can be very rapid.

Thus, there is substantial diversity in the suggested mechanisms of stress-corrosion cracking in titanium alloys. It can probably be stated that the diversity of the reactions that can possibly occur when titanium alloys are exposed simultaneously to tension stress and various environments suggests that the term stress-corrosion cracking may be regarded as generic, encompassing a number of specific mechanisms. This does not minimize the importance of establishing conclusively the role played by hydrogen, where conflicting models (including a hydrogen

mechanism) have been proposed to explain stress-corrosion cracking of titanium alloys in the same environment.

EXPERIMENTAL APPROACH

In this section, an experimental approach will be outlined in an attempt to delineate the role played by hydrogen in the stress-corrosion cracking of titanium alloys. It has already been shown that hydrogen by itself can produce in titanium alloys (and other alloys, such as steel) a cracking process having all the physical appearances of stress-corrosion cracking. The obvious question that arises is whether the cracking that occurs in aqueous and other environments is by anodic reaction of conventional stress-corrosion cracking or directly because of the cathodic reduction of hydrogen, i.e., hydrogen embrittlement.

A number of questions on both types of cracking are under consideration, namely: In hydrogen-charged material, where is the hydrogen located? Is hydrogen movement induced by a stress or concentration gradient? How does the crack growth process occur? In stress-corrosion cracking, where does the microcrack first form? Can the two processes even be in some way complementary to each other?

MATERIALS

It is suggested that preliminary investigations be restricted to titanium-aluminum-based, all-alpha alloys. Since aluminum is known to alter (38, 40) the dislocation structure of alpha solid solution, at this stage of experiment the amount of aluminum should be held constant and should not exceed 5 wt% in order to minimize the tendency of ordering in the microstructure. Also, since interstitial oxygen acts in much the same way as aluminum and promotes stress-corrosion cracking, the oxygen content should be kept at the minimum level possible. A Ti-5Al-2.5Sn (41) alloy with low oxygen content would be a suitable alloy for investigation.

Another alloy, e.g. Ti-13V-11Cr-3Al solution treated and quenched to give an all-beta structure, should also be investigated in order to compare and contrast the role of hydrogen on the stress-corrosion cracking of the hexagonal, close-packed alpha and the body-centered, cubic beta solid solutions.

Finally, an alpha-beta alloy should be considered. The Ti-13V-11Cr-3Al alloy can be aged below the beta transus to give an alpha-plus-beta structure. The amount of alpha can be varied by appropriate choice of aging temperature and time.

ENVIRONMENTS

Specimens will be investigated both in the hydrogen-charged condition (by heat treatment in a closed atmosphere of hydrogen) and in the uncharged condition. The tests should be conducted in both liquid, e.g. aqueous chloride and methanol-water vapour, and gaseous, e.g. dry air, helium, and hydrogen gas environments.

TECHNIQUES

Specimen Geometry

Most of the tests should be conducted with sustained load notched flat tensile tests, as they have been shown to be most useful in revealing the stress-corrosion susceptibility. Notch bend tests should also be conducted using Charpy specimen geometry.

Since stress-corrosion resistance generally varies with grain orientation, all the tensile specimens should have the same orientation relationship between the texture of the wrought sheet and the tension axis, in order to minimize the anisotropy effects. Since in alpha alloys of titanium the cleavage plane is generally described by a 12- to 14-deg rotation from the basal plane, it is suggested that these specimens be oriented to make the tension axis approximately perpendicular to the cleavage plane, in order to facilitate the propagation of stress-corrosion cracks.

The specimen must be thick enough so that the effects of plane stress zone are negligible. At present the most conservative estimate, given by Brown et al. (42), is that the thickness should not be less than about $2.5 (K/\sigma_y)^2$, where K is the stress intensity and σ_y is the yield strength.

Crack Growth Rate

The rate of propagation of stress-corrosion cracks depends upon the stress intensity K . Hence, a proper characterization of the stress-corrosion-cracking behavior of a given system would require determination of crack growth kinetics at all K levels up to K_{IC} . The different methods for monitoring crack growth have been summarized by Brown (43). It is suggested that (1) measurements of the yawning of the crack be made using a resistometric crack-opening clip gage inserted in the crack, or (2) crack growth be monitored using an ultrasonic monitoring device. The latter method requires a demonstration that it does not influence the cracking process, and it also requires an empirical calibration. To establish if a true K_{ISCC} exists, the specimen configuration termed a "wedge-force specimen" could be used to minimize the total number of tests required. This has been described by Smith et al. (44) where the specimen is loaded to a stress intensity factor less than K_{IC} but higher than the expected K_{ISCC} . As the crack grows under constant load, the net section stress increases but K decreases, until finally the crack growth rate decreases to an apparently arrested condition.

Details of Cracking Phenomenon

The great progress in recent years in the understanding of the process of cracking has been due to the application of the electron microscope by way of electron fractography and thin-foil transmission electron microscopy. These studies provide a strong connecting link between the imperfection structure of the alloy, the distribution of crystallographic phases and other microstructural details, and the distribution of various crystallographic species on the fracture surface, which provides the least resistant path.

Examination of fracture surfaces by the extraction replica technique has been found to be extremely useful in differentiating between mechanical fractures that are generated by microvoid coalescence and typical stress-corrosion cracks which nucleate at the surface and have the general characteristics of a cleavage fracture. But it should be pointed out that the relative proportion of cleavage and mechanical rupture in some titanium alloys (45) is a function of the ratio of the initial crack tip stress intensity parameter to the plane stress fracture toughness parameter—a high ratio increasing the proportion of mechanical rupture.

Application of electron diffraction, X-ray diffraction, and electron microprobe analysis would also be used whenever possible to characterize the metallurgical species lying along the crack plane and also to characterize the fracture path itself. Mention should be made of the technique of micro-autoradiography developed by Tiner and coworkers (31), which appears to be a potent tool for investigating the possibility of hydrogen segregation to the environmental cracks forming in the stable-growth range as well as in determining the permeability of surface films to specific ions.

The following gives a general outline of investigations that could be conducted to delineate the role of hydrogen in the stress-corrosion cracking of titanium alloys. Because of the complexity of the process, it is unlikely that an experiment can be easily designed to establish decisively whether or not hydrogen plays a role. Therefore, these studies should be regarded as exploratory at present. Throughout this exploratory stage, studies of the effect of such variables as stress intensity, temperature, and environments on the kinetics of crack growth will form an important part of the investigation.

1. Careful examination by electron microscopy has revealed that stress-corrosion cracks nucleate at the surface-corrodent interface, whereas hydrogen-corrosion embrittlement nucleates beneath the

surface in the zone ahead of the crack tip and spreads toward the tip. Similar experiments can be conducted with edge-notched titanium alloys in different environments to establish the exact location at which the crack nucleates. If the crack is found not to nucleate at the specimen-corrodent interface, then conventional theories of stress-corrosion cracking, including brittle-film theories, are not the primary mechanism for that system.

2. Logan and Yolken (46), using hollow notched tensile steel specimens, showed that hydrogen diffusion into the steel was at least 50 times greater in an acetic acid-hydrogen sulfide environment than in an ammonium nitrate environment. The hollow specimen was connected to the vacuum system through the pull rod. Valves divided the vacuum system into three sections: the pumping system, a section for collecting gas samples and measuring pressure, and the specimen section. The specimen under tension was evacuated to a pressure of less than 5 microns, the pumping system was disconnected, the rate of pressure increase in the remainder of the system was determined by a pirani gage, and the percentage of hydrogen in the system determined by a mass spectrographic technique. It is suggested that Logan's experiment be repeated with titanium alloys in the environments mentioned earlier.
3. Recently, a relationship has been shown between the hydrogen content of certain titanium alloys and the susceptibility to stress-corrosion cracking of these alloys in salt water. If hydrogen in the alloy is involved in stress-corrosion cracking, one might also look for the "delayed fracture" type of failure, which hydrogen is known to cause in certain steels.

Occurrence of such "delayed fracture" has been established by Sandoz and Newbegin (47) in a Ti-8Al-1Mo-1V alloy containing 48 to 50 ppm hydrogen. But the effect of varying the hydrogen content has so far been inadequately investigated. It is therefore suggested that the susceptible Ti-5Al-2.5Sn alpha alloy be changed to a different level of hydrogen content. Experiments should be conducted to ascertain whether an embrittlement exists and, if so, whether it is a function of hydrogen content. The tests would be conducted in dry air and dry helium. The characteristics of the fracture surface would be investigated with electron fractography. Experiments should also be conducted to ascertain whether a threshold stress intensity level exists and, if so, whether it could be raised by prior and progressive degassing treatments in vacuum to alter the hydrogen content.

4. Studies (48) of crack growth rates and stress-wave emission and fractographic studies on high-strength steel indicate that hydrogen-induced and distilled-water-induced failures involve essentially the same slow crack growth process.

Similar experiments can be repeated, particularly with the titanium alloy, using an accelerometer technique to monitor the stress waves given off by discontinuous crack extension. This would allow an estimate of the amount of crack growth in each discontinuous movement, as well as providing information about the time-dependent mechanism involved between crack steps. A crack-opening displacement gage can be used to determine instantaneously the crack length at a given time, enabling crack growth rates and stress intensity factors to be described during the test.

The experimental approach would be to evaluate slow crack growth in titanium alloys by (1) testing in the hydrogen-charged condition, (2) testing nonhydrogenated samples in methanol-water vapor environments, and (3) testing hydrogenated samples in methanol-water vapor environments.

It is important to establish that monitoring of stress waves does reflect slow crack growth. Earlier work had shown that stress-corrosion cracking by dissolution in a copper alloy resulted in no significant increase in acoustic emission when compared with the nonenvironmental tests. But Gerberich et al. (48) observed in acoustic emission studies that crack propagation in hydrogen-embrittled steel was a discontinuous process. Hence, if stress-wave emission is to give information concerning stress-corrosion cracking, the mechanism must at least partially involve a brittle-crack-step process rather than merely a dissolution mechanism.

Another important observation would be the individual effects versus the combined effects of hydrogenation and methanol vapor. If one or the other cracking mechanism is rate controlling, then the combined effect would be expected to be less than the sum of the individual crack growth rates. On the other hand, if the cracking mechanisms reinforce each other, one may expect the combined effect to be greater than the sum of the individual crack growth rates. [Such a synergistic effect has been noted in high-strength steel (48).] Recent work of Sandoz et al. (47) has shown that for Ti-8Al-1Mo-1V alloy, the threshold stress intensity K_{ISCC} for slow crack growth in salt water or methanol vapor environments is not affected by varying the

hydrogen content from about 5 to 50 ppm and is approximately $25 \text{ ksi}\sqrt{\text{in.}}$. But the threshold stress intensity K_{IH} for slow crack growth in air decreases from 100 ksi to about $40 \text{ ksi}\sqrt{\text{in.}}$ over the same variation of hydrogen content. It would be interesting to see if this trend persists at progressively higher levels of hydrogen content and if, finally, the K_{ISCC} and K_{IH} curves cross over. Most likely the K_{IH} curve will intersect the K_{ISCC} curve at a specific hydrogen content and, beyond that, the K_{IH} and K_{ISCC} values will be similar and equal to the original K_{ISCC} value. If this is the case, then studies of crack growth rates in specimens having a hydrogen content that represents a threshold for both K_{ISCC} and K_{IH} may indeed reveal a synergistic effect.

5. Studies of the temperature sensitivity of the stress-corrosion process can be conducted to establish the activation energy of the crack growth process. Since stress-corrosion-crack growth rates often are sensitively affected by the stress intensity parameter K , estimates of activation energy from growth rates must be made at constant values of K . Such studies of activation energies can be made using several approaches, such as:
 - Crack growth in a methanol-water vapor environment
 - Time for, say, 50-percent recovery of fracture stress after cathodic charging (care should be taken to avoid formation of distinct hydride phase)
 - Incubation period for crack initiation in cathodically charged specimen.
 - Crack growth in hydrogenated specimens

The detailed experimental setup for these investigations will call for careful planning. The experimentally deduced activation energies would be compared with the data on thermally activated bulk diffusion of hydrogen in titanium, as well

as with the results from internal friction measurements on stress-induced interstitial diffusion of hydrogen in titanium.

If the experimental activation energies compare favorably with those for hydrogen diffusion, it would provide strong support for hydrogen as the embrittling agent. The comparison of activation energies in (1) hydrogenated and (2) nonhydrogenated external methanol-water vapor environments is designed to test if the source and distribution of hydrogen at the time of stress application has any effect on the mechanism of embrittlement.

6. Recently a striking brittleness associated with an external environment of molecular hydrogen at atmospheric pressure has been demonstrated (49) in high-strength steel. It is extremely unlikely in this case, however, that the embrittlement is due to pressure buildup inside any voids in steel.

The influence of oxygen in vapor environments upon subcritical crack growth has been studied by Hancock and Johnson (49). They investigated for crack growth in environments containing varying proportions of argon, water, nitrogen, water vapor, hydrogen, and oxygen. As little as 0.6 percent oxygen was sufficient to terminate subcritical crack growth in steel specimens in vapor environments. An oxygen-stopped crack could be restarted only when oxygen was removed from a gaseous environment.

The above experiments strongly suggest that the crack tip surface must absorb oxygen in preference to hydrogen and water vapor. This is consistent with the well-known affinity of iron for oxygen. Presumably when the oxygen supply is removed hydrogen may reduce the oxide, whereas water and water vapor may

either supply hydrogen or perhaps dissolve the oxide.

Titanium has a strong affinity for oxygen, as evidenced by the large negative free energy of formation of titanium dioxide. Experiments would be conducted to ascertain if chemisorption of hydrogen can indeed occur in titanium alloy at a clean oxygen-free surface (this is generally provided at the stressed crack tip) to produce embrittlement. If an embrittlement is observed, then investigations of crack growth, in environments containing different proportions of gases including hydrogen and oxygen, would be conducted to test the validity of hydrogen-reduction hypotheses.

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